XXII. Observations on Arragonite, together with its Analysis. By the Rev. John Holme, A.M. F. L.S.

Read April 6, 1813.

THERE is no substance, which has of late years more excited the attention of chemists and mineralogists, than Arragonite, so called from the place where it was originally discovered. As the only anomaly in the Abbe Hauy's Theory of Crystallization, it has long been suspected that in its chemical analysis it would be found to differ from the carbonates of lime, with which it has been hitherto classed. This suspicion has been augmented by other circumstances of external character, beside those of crystallization and mechanical division. It is much harder than any of the common crystallized carbonates of lime, so as to scratch them easily. Its specific gravity is also greater, being 2.9465*, instead of 2.718+, which is the specific gravity of common calcareous spar. Yet the most careful analysis of Arragonite has not brought to light any fact at variance with the received opinion concerning its composition. "The difference in its primitive form," it is said, "does not result from any difference in its chemical combination t."

Under these circumstances I was induced to undertake the analysis of Arragonite. The result, I trust, will prove that it is not, as has been so often asserted, a pure carbonate of lime; and

that,

^{*} Haüy. † Thomson's Chemistry, vol. iv. ed. 4, p. 347.

[‡] Brongniart's Mineralogy, vol. i. p. 222.

that, therefore, it ought not to be considered as constituting any anomaly in the theory of Haüy; which admits a difference of structure, or of mechanical division, whenever there is a change in the constituent parts of a simple mineral.

The difficulty of obtaining good specimens of Arragonite for some time delayed my experiments; but having at last procured some very fine hexahedral crystals of that mineral, I selected the purest parts of these, and proceeded in their analysis.

My observations were the following: A moderate degree of heat, when applied to a small fragment of Arragonite, is sufficient to reduce it to a white, opaque powder. The substance at the same time loses part of its weight. The volatile matter which makes its escape produces no decrepitation, but passes off silently, in a manner similar to that of carbonic acid when expelled by heat from chalk or limestone.

Experiment 1.—In order to ascertain the nature of this volatile matter, I made the following experiment: A small glass bulb furnished with a narrow tube was filled with 205 grains of Arragonite coarsely powdered; but previously both the powder and vessels had been exposed to the heat of the sun, for the purpose of driving off any moisture which might adhere to their surfaces. The bulb was then imbedded in a crucible filled with dry sand, and placed in an open furnace containing a charcoal fire. The tube of the bulb was bent in such a manner, that its extremity could easily be brought under the orifice of an inverted glass tube filled with mercury. The fire surrounding the crucible was gradually raised, care being taken not to expose the subject to too high a temperature, for fear of separating the carbonic acid from its base. In the space of about thirty minutes an elastic fluid was collected over the mercury, causing it to descend about an inch and a half. The mercurial trough, &c. were now removed into a

cold situation; and as the inclosed air acquired the temperature of the surrounding medium, the interior of the glass tube, occupied by it, became gradually covered with moisture, which at length ran down in striæ. Now, as the vessels, and the substance contained in the bulb, were carefully freed from superficial moisture, the water could only be derived from the Arragonite used in the experiment. Lime-water was then admitted to the air confined over the mercury, but produced no precipitate. Hence it is evident that carbonic acid gas was not present, at least in any sensible quantity. On a further examination of this clastic fluid, it was found to be merely atmospheric air, which had been expanded out of one vessel into the other during the operation. Thus it appears that Arragonite, when exposed to a degree of heat inferior to that which is requisite to calcine it, gives out water, and, at the time of its expulsion, reduces the calcareous substance to a white, opaque powder, and that without decrepitation*. Hence it is inferred that the water contained in the mineral is chemically combined with its constituents; for, if otherwise, it would exhibit the same phænomenon of decrepitation which attends the extrication of water from calcareous spar, when exposed to the action of heat.

Experiment 2.—When water is present in common calcareous spar, it occupies only certain interstices, from which it may be easily expelled at a low temperature, and even without affecting its general transparency. Arragonite, on the contrary, when deprived of its aqueous particles by a slight degree of heat, loses all its transparency; from which it may be concluded that these

^{*} The analyses of Arragonite and of calcareous Spar, by Thenard and Biot, show that the quantity of water contained in the former exceeds that of the latter.—Mem. d'Arcueil, ii. 176.

particles are chemically combined with the constituents of the mineral, being uniformly diffused through the whole mass.

Experiment 3.—One small specimen of calcareous spar, and another of Arragonite, about the same size, were placed at the same instant on a plate of iron heated to redness. The thickness of the plate somewhat exceeded half an inch. The former specimen began almost immediately to decrepitate and disperse, whilst the other remained unaltered; but afterwards acquiring a greater degree of heat, the Arragonite fell gradually to powder. This experiment proves that the water is retained more strongly in the Arragonite than it is in the calcareous spar; from which circumstance the same inference may be made as before, viz. that water is chemically combined in the Arragonite, and only mechanically mixed in the other substance. This operation I have frequently repeated with the same result, and also in a manner more precise as to the degree of heat required for expelling the water from each kind of calcareous spar.

Experiment 4.—I took a part of a crystal of Arragonite, and, fixing it to the end of a wire, plunged it into boiling mercury, and kept it there for some time. Upon withdrawing it, no change had taken place, the spar coming out unbroken, and with its original transparency.

Experiment 5.—I then took a piece of common calcareous spar, which was part of a stalactite, and plunging it in the same manner as before into boiling mercury, it instantly decrepitated and flew to pieces.

Experiment 6.—Gypsum also tried in the same way lost its water of crystallization, which, as it was some time in coming away, gave to the mercury the appearance of violent ebullition from the escape of the water under it in the state of vapour.

Experiment 7.—The water that is contained in the Arragonite being chemically combined with the lime and carbonic acid, may occasion a closer union in those parts; and this I have in some measure verified by taking the specific gravity of Arragonite after its desiccation. It proved to be 2.727 instead of 2.94, which was its original specific gravity; and at the same time, by a similar mode, the specific gravity of Iceland crystal was 2.732. This near equality of specific gravity in the two bodies is sufficient to show that Strontian earth does not enter into the composition of Arragonite, as has been lately advanced by a German chemist.

ANALYSIS.

Some transparent crystals of Arragonite were reduced to powder, which was dried in the sun, to be certain of not overheating it.

Twenty grains of this powder were weighed, and wrapped up in a clean thin leaf of platinum, that no part of it might be lost. The weight of the platinum was previously determined. The Arragonite thus folded up was placed on a plate of iron heated red-hot, and, after remaining in that situation for a short time without any of the carbonic acid being expelled, was carefully weighed in an excellent balance, and the inclosed substance was then found to have lost 0.16 grain of volatile matter, which has been already proved to be water. I made several experiments of this kind, but without observing any difference in the results.

The substance inclosed in the leaf of platinum was afterwards kept in the fire till it had acquired a dull red heat. The loss of weight, when accurately ascertained, = 0.25 grain. This additional diminution of weight cannot, I think, be ascribed to a further loss of water, because in this experiment a thin piece of Iceland crystal, which had been wrapped up together with the Arragonite, (but taken out before the deficit in weight was estimated,)

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and of course subjected to the same degree of heat, was super-ficially calcined. Hence it is concluded that the Arragonite which accompanied it had undergone the same process, and parted also with a portion of its carbonic acid. On this account, it is probable that the weight of water in 20 grains of the substance analysed cannot be far different from that which has been already stated, viz. 0.16 grain.

The 20 grains of Arragonite contained in the leaf of platinum were put into the bowl of a tobacco-pipe, which had a cover fitted to it, and exposed to a strong heat till the calcareous substance was thoroughly calcined. The lime weighed whilst warm 11.16 grains: consequently the weight of the volatile matter driven off = 8.84 grains. But the weight of water in 20 grains of Arragonite = 0.16 grain. The weight, therefore, of the carbonic acid will = 8.68, or per cent.

Lime - = 55.80Carbonic acid - = 43.40Water - = 0.80 = 100 grs.

It does not seem, therefore, unreasonable to conclude that the water, since it appears to be an essential part of the composition of Arragonite, should produce that variation of specific gravity, hardness, and crystalline form, which distinguishes it from the common crystallized carbonates of lime. For though the quantity of water be not agreeable to the usual proportions in which bodies have been observed generally to unite; yet there are instances where great changes are produced by similarly small additions of a foreign ingredient. A very striking one, among many others which might be noticed, is in the change of iron to steel, which is effected by a quantity of carbon as small in proportion to the iron as that of the water in the Arragonite.

Analyses of Arragonite and of calcareous Spar by MM. Thenard and Biot. Mem. d'Arcueil, ii. 176.

	Arragonite.		Calcareous Spar.
Lime -	= 56.351	-	= 56.327
Carbonic Acid	= 42.919		= 43.045
Water -	= 0.730	-	= 0.625
	100.000		100.000

Note,—Since the above observations were written, it has been again asserted, that the presence of Strontian in Arragonite has been ascertained by the German chemist before mentioned in p. 239, not as an adventitious mixture, but as an essential constituent. In answer to which I have only to observe, that in the specimens of Arragonite which I have subjected to analytical examination, I have never detected an atom of Strontian. Of course every thing must depend upon the purity of the specimens selected by the German Professor for his experiments.

Cambridge, November 4, 1814.